

AD-A274 419



OFFICE OF NAVAL RESEARCH  
Grant No. N00014-91-J-1655  
R&T Code 4132058---02

TECHNICAL REPORT NO. 20

Kinetics of 2-Pentadecylaniline Polymerizations in Monolayers:  
Relationships Between Experimental Data  
and a New Theoretical Model

by

Raj Bodalia and Randolph Duran

Center for Macromolecular Science and Engineering  
Department of Chemistry  
University of Florida  
Gainesville, FL

José Manzanares

Departamento de Termodinamica  
Facultad de Fisica  
Universidad de Valencia  
46100 Burjasot, Spain

and

Howard Reiss

Department of Chemistry  
University of California at Los Angeles  
Los Angeles, CA 90024

DTIC  
ELECTE  
JAN 05 1994  
S E D

93-31598

3808

Reproduction in whole or in part is permitted for any purpose of the  
United States Government.

This document has been approved for public release and sale; its  
distribution is unlimited.

REPORT DOCUMENTATION PAGE			Form Approved OMB No 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503</small>				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 12/9/93		3. REPORT TYPE AND DATES COVERED
4. TITLE AND SUBTITLE Kinetics of 2-Pentadecylaniline Polymerizations in Monolayers: Relationships Between Experimental Data and a New Theoretical Model.			5. FUNDING NUMBERS Grant No. N00014-91-J-1655	
6. AUTHOR(S) Raj Bodalia, Randolph Duran, Jose Manzanares, and Howard Reiss				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) R. S. Duran Department of Chemistry University of Florida Gainesville, Florida 32611			8. PERFORMING ORGANIZATION REPORT NUMBER 20	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Dr. Kenneth J. Wynne Code 1113PO, Office of the Chief of Naval Research 800 North Quincy Street Arlington, VA 22217-5000 (703) 696-4409			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  In this paper we have presented a simple theoretical model that provides a detailed understanding of aniline polymerization kinetics in a monolayer. Even though the model is primitive, it agrees very well with our experimentally measured data. The rate constant and activation energy obtained in our previous study from the modified Gee and Rideal equation have been found as geometric and arithmetic means, respectively, of values which correspond to the initiation and propagation steps. This model allows us to predict an average degree of polymerization and thus an average molecular weight and the fraction of reacted monomer at any stage during the polymerization reaction. Also, some predictions regarding the temperature dependence of molecular weight can be made from this model.				
14. SUBJECT TERMS			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified
20. LIMITATION OF ABSTRACT				

# Kinetics of 2-Pentadecylaniline Polymerizations in Monolayers: Relationships Between Experimental Data and a New Theoretical Model

Raj Bodalia<sup>a</sup>, Jose' Manzanares<sup>b</sup>, Howard Reiss<sup>c</sup>, and Randolph Duran<sup>a</sup>

(a) Department of Chemistry, Center for Macromolecular Science and Engineering, University of Florida, Gainesville, FL 32611-2046

(b) Departamento de Termodinamica, Facultad de Fisica, Universidad de Valencia, 46100 Burjasot, Spain.

(c) Department of Chemistry, University of California at Los Angeles, Los Angeles, California 90024

DTIC QUALITY INSPECTED 8

## ABSTRACT

In this paper we have presented a simple theoretical model that provides a detailed understanding of aniline polymerization kinetics in a monolayer. Even though the model is primitive, it agrees very well with our experimentally measured data. The rate constant and activation energy obtained in our previous study from the modified Gee and Rideal equation have been found as geometric and arithmetic means, respectively, of values which correspond to the initiation and propagation steps. This model allows us to predict an average degree of polymerization and thus an average molecular weight and the fraction of reacted monomer at any stage during the polymerization reaction. Also, some predictions regarding the temperature dependence of molecular weight can be made from this model.

or	
&l	<input checked="" type="checkbox"/>
sd	<input type="checkbox"/>
Distribution /	
Availability Codes	
Dist	Avail and / or Special
A-1	

## INTRODUCTION

Among all conducting polymers, polyaniline is among the most studied material due to its electrical conducting properties and good thermal stability in the presence of oxygen and moisture.<sup>1-3</sup> It is structurally unique in that nitrogen atoms occupy the bridging position in its backbone and are a part of the  $\pi$  structure. It is also unique among all conducting polymers in that its electrical properties can be controlled both by the main chain oxidation state and the level of protonation.<sup>4,5</sup> Polyaniline exhibits multiple color changes depending on both oxidation state and pH.<sup>6-8</sup> The above features have resulted in a number of potential applications.<sup>9-14</sup>

Polyaniline and its derivatives are usually synthesized by standard techniques in isotropic media. It can be prepared chemically using different oxidizing agents<sup>15-19</sup> or electrochemically in aqueous or non aqueous media.<sup>20-24</sup> Some o-substituted anilines have also been polymerized at an air-water interface using the Langmuir-Blodgett (LB) technique.<sup>25-28</sup> In this technique a reaction occurs under anisotropic conditions caused by the surface induced orientation of the monomer, and the polymer chains in the resulting monolayer may have enhanced long range configurational, orientational, and positional ordering and greater anisotropic properties than polymers synthesized by conventional methods.

Although a large number of papers have been published on the preparation of polyaniline and its properties, the kinetics of polymerization and the corresponding mechanism are still under discussion. Even though a complete description of aniline polymerization kinetics clearly involves

several rate constants, published work has described only two rate constants and a detailed theoretical treatment is lacking. In the electrochemical polymerization of aniline, Wei, et al.<sup>29</sup> proposed that the overall rate of polyaniline formation depends on at least two rate constants, a constant for initiation ( $k_i$ ), and one for the rate of propagation ( $k_p$ ).  $k_i$  is the rate constant before polymer is formed on the electrode while  $k_p$  is the rate constant when polymer exists on the electrode. Since  $k_i$  is much smaller than  $k_p$ , the initial rate constant was neglected in calculations of the polymerization rate and activation energy. Gregory, et al. also used a similar kinetic model for the chemical polymerization of aniline in aqueous solutions.<sup>30</sup>

Recently our group has adopted the monolayer polymerization approach as a possible means of understanding aniline polymerization kinetics.<sup>31</sup> In this study the equation derived by Gee and Rideal<sup>32-34</sup> was used to determine a single rate constant. This constant was calculated from the maximum value of the average barrier speed and the corresponding mean molecular area. However, this equation is very simple and does not account for some of characteristics of the polymerization mechanism described above. In particular, there is no consideration of the important difference between the rate constants for the initiation and propagation. The aim of this paper is (1) to construct a theoretical model for the polymerization kinetics involving a rational formulation of the rate equations using at least two constants, (2) to establish relationships between the experimental results and the theory in order to calculate and interpret  $E_a$  at different stages of the polymerization, (3) to use this information to predict a molecular weight at any temperature and at any time during the

Langmuir polymerization reaction, and (4) to discuss the reaction rate constant and activation energy obtained from the modified Gee and Rideal equation.

## EXPERIMENTAL

The synthesis of the 2-pentadecylaniline used in the study of the monolayer polymerization kinetics is reported elsewhere.<sup>35</sup> Polymerization was carried out at constant applied surface pressure in a commercial Langmuir trough LB-5000 (KSV Instruments, Finland) equipped with a computerized control and one or two barriers. Surface pressures were measured using the Wilhelmy plate film balance method with a platinum plate that was carefully pre-wetted and zeroed in clean sub-phase prior to measurement. The interior trough surfaces and the barrier were made of Teflon. The trough and sub-phase temperature was controlled (to  $\pm 0.1^\circ\text{C}$ ) by passing water from a constant temperature bath through channels below the trough. The sub-phase temperature was measured with either a calibrated thermometer or a Teflon coated thermocouple.

In all polymerization experiments, monomer was spread on a sub-phase consisting of a homogeneous mixture of 0.1M  $\text{H}_2\text{SO}_4$  and 0.03M  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . Ammonium persulfate acts as an oxidizing agent and has been used for chemical polymerization of aniline and its derivatives. After spreading the monomer solution, the solvent (chloroform) was allowed to evaporate from the interface for 2 minutes. The resulting monolayer film was then compressed ( $90 \text{ \AA}^2\text{molecule}^{-1}\text{min}^{-1}$ ) until the desired applied surface pressure was reached. The surface pressure was maintained constant during the entire reaction by moving the barrier, and the reaction was monitored either by measuring the change in mean molecular area or the average barrier speed. The zero of reaction time was taken as the point at which the surface pressure reached a desired value.

Polymerization experiments were repeated at least three times. The reproducibility of both the time at which the maximum barrier speed was achieved and its magnitude under given conditions was typically better than  $\pm 2\%$ .



## THEORY AND RESULTS

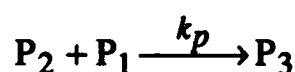
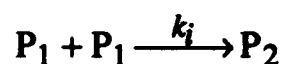
Typical curves for the polymerization of 2-pentadecylaniline at the air-aqueous interface are shown in Figure 1. In this figure, the mean molecular area and the average barrier speed are plotted versus time. A monotone decrease in the mean molecular area was observed during the polymerization reaction. This is due to the replacement of van der Waal's radii by covalent bonds between monomer molecules, and changes in their conformation.<sup>25,26</sup> The average barrier speed increased from an initial value of zero, reached a maximum, and then decreased to zero (or negligible value). When the mean molecular area achieved a constant value or the average barrier speed dropped to zero, the reaction was considered complete.

Figure 1.

Polymerization is initiated by the activation of monomer molecules through the formation of a radical cation intermediate. This process involves monomer protonation by sulfuric acid and oxidation by persulfate ions, both diffusing to the surface from the bulk subphase. As a result the polymerization reaction is not strictly two-dimensional. The initiation step is followed by the coupling of two radical cations to form a dimer (referred to in the subsequent text as initiation) which constitutes the rate-determining step in the polymerization process. The dimer and all other oligomers (including the polymers) have lower oxidation potentials than monomer<sup>29</sup> and have the ability to catalytically oxidize a neutral aniline molecule. Thus, polymerization occurs via oxidation of the growing polymer chain and the addition of an activated monomer molecule

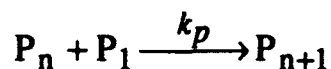
(referred to in the text as propagation), in such a way that every addition is easier than the previous one. The products from either the initiation or propagation steps must then be re-activated before another reaction can occur. In principle, polymerization could also occur through the coupling of oligomers and longer species. However, we do not consider such coupling since (1) in a surface reaction the oligomers are sterically trapped and diffuse slowly compared to a monomer making it less probable for an oligomer to find another oligomer rather than an unreacted monomer, (2) such coupling would have to be head-to-head, a process that is known to be negligible under highly acidic conditions<sup>23</sup> and also, in our case, sterically unfavorable, and (3) it has been shown in both the solution<sup>36</sup> and the monolayer<sup>37</sup> that the molecular weight versus conversion is similar to that of a chain growth mechanism, and not to one of step growth. The activation of isolated monomer molecules is not very likely, but the presence of polymer chains considerably increases the rate of this step.<sup>38</sup> The self-catalysis of the polymerization process will then result in an activation energy for the propagation much smaller than for the initiation. Thus, our simplified approach will incorporate two rate constants:  $k_i$  for initiation and  $k_p$  for propagation, the latter being much larger than the former.

In view of the above facts, we suggest the following approximate for a chain polymerization



.....

(1)



where  $P_n$  denotes a polymer chain composed of  $n$  monomer units or an  $n$ -mer ( $P_1$  denotes monomer), and  $k_i$  and  $k_p$  are the rate constants for initiation and propagation, respectively. It must be recalled that the incorporation of a monomer molecule by a polymer chain takes place only after oxidation of both the monomer and the chain end. Since the oxidation of long chains is easier than that of shorter chains, monomer addition is easier for the former, and chains of different length will have different rate constants for propagation such that  $k_{p(n+1)} \geq k_{p(n)}$ . Polymerization kinetics with non-equal propagation constants have already been discussed in the literature<sup>39,40</sup> and could be included in our study. However, in our case we assume that this effect will not be very noticeable because chain oxidation is not the slow step in the addition of monomer to the chain. Alternatively, monomer activation will very likely be the rate-determining step. Therefore in the following, a single value for the propagation rate constant,  $k_p$ , will be used.

The rate equations corresponding to the steps shown in (1) are

$$\begin{aligned} \frac{dN_1}{dt} &= -2k_i N_1^2 - k_p N_1 \sum_{i=2}^{\infty} N_i \\ \frac{dN_2}{dt} &= k_i N_1^2 - k_p N_1 N_2 \\ \frac{dN_n}{dt} &= k_p N_1 N_{n-1} - k_p N_1 N_n, \quad n \geq 3 \end{aligned} \tag{2}$$

where  $N_n$  represents the number of  $n$ -mer molecules. The initial conditions are

$$N_1(0) = N, \text{ and } N_n(0) = 0 \text{ for } n \geq 2. \quad (3)$$

Introducing the new independent variable (a reduced time)

$$\tau = \int_0^t N_1 dt \quad (4)$$

into eq. (2), transforms them into a system of ordinary linear differential equations, namely

$$\begin{aligned} \frac{dN_1}{d\tau} &= -2k_i N_1 - k_p \sum_{i=2}^{\infty} N_i \\ \frac{dN_2}{d\tau} &= k_i N_1 - k_p N_2 \\ \frac{dN_n}{d\tau} &= k_p N_{n-1} - k_p N_n, \quad n \geq 3 \end{aligned} \quad (5)$$

This system can now be solved by means of a Laplace transformation and the solution of the resulting linear system of algebraic equations. However, it is simpler to rewrite eq. (5) in terms of  $N_1$  and the variable

$$\theta = \sum_{i=2}^{\infty} N_i \quad (6)$$

The resulting system of equations is two in number. These are

$$\frac{dN_1}{d\tau} = -2k_i N_1 - k_p \theta, \text{ and } \frac{d\theta}{d\tau} = k_i N_1 \quad (7)$$

and they can easily be solved simultaneously to yield

$$\begin{aligned} N_1(\tau) &= N e^{-k_i \tau} \left\{ \cos(k\tau) - \frac{k_i}{k} \sin(k\tau) \right\} \\ \theta(\tau) &= N \frac{k_i}{k} e^{-k_i \tau} \sin(k\tau) \end{aligned} \quad (8)$$

where

$$k = \sqrt{k_i(k_p - k_i)} \quad (9)$$

and will be denoted hereinafter as the (*geometric*) average rate constant for the polymerization process.

Before proceeding further, we introduce two observables of well-known experimental relevance - namely, the number-average and the weight-average molecular weights. These are defined, respectively, as

$$\bar{M}_n = M_1 \frac{\sum_{i=1}^{\infty} i N_i}{\sum_{i=1}^{\infty} N_i} = M_1 \frac{N}{N_1 + \theta} \quad (10)$$

and

$$\bar{M}_w = M_1 \frac{\sum_{i=1}^{\infty} i^2 N_i}{\sum_{i=1}^{\infty} i N_i} = M_1 \frac{\sum_{i=1}^{\infty} i^2 N_i}{N} \quad (11)$$

where  $M_1$  is the molecular weight of the monomer molecule. Then, eq. (8) allow for a straightforward calculation of  $\bar{M}_n$ , but not of  $\bar{M}_w$ , which is often the more interesting of the two. In order to calculate  $\bar{M}_w$ , we make use eq. (5) and obtain its time derivative by multiplying by  $i^2$  and summering the resulting equations. The result is

$$\frac{d\bar{M}_w}{d\tau} = \frac{M_1}{N} \frac{d}{d\tau} \left[ \sum_{i=1}^{\infty} i^2 N_i \right] = \frac{2M_1}{N} [k_i N_1 + k_p (N - N_1)] \quad (12)$$

which can be integrated, using the first of eq. (8), to yield

$$\overline{M}_w = M_1 \left[ 1 + 2k_p \tau - 2 \frac{k}{k_i} e^{-k_i \tau} \sin(k\tau) \right] \quad (13)$$

So far we have obtained  $N$ ,  $\theta$ ,  $\overline{M}_n$ , and  $\overline{M}_w$  as functions of  $\tau$ . These quantities could be expressed as a function of time  $t$  by using eq. (4) and solving for  $t$  as

$$t = \int_0^{\tau} \frac{d\tau}{N_1(\tau)} \quad (14)$$

Unfortunately, the integral in eq. (14) cannot be evaluated analytically, but we can get some insight into the behavior of the system without resorting to numerical integration. Indeed, it is clear from eq. (14) that the end of the reaction ( $t \rightarrow \infty$ ) will correspond to a finite value of  $\tau$  given by the condition  $N_1 = 0$ . This value will be denoted by  $\tau_\infty$  and can be obtained from eq. (8) as

$$\tau_\infty = \frac{1}{k} \arctan \frac{k}{k_i} \quad (15)$$

The number- and weight-average molecular weight at the end of the reaction can now be calculated by introducing eq. (15) into eqs. (10) and (13), yielding

$$(\overline{M}_n)_\infty = M_1 \sqrt{\frac{k_p}{k_i}} \exp \left[ \frac{k_i}{k} \arctan \frac{k}{k_i} \right] \quad (16)$$

and

$$(\overline{M}_w)_\infty = M_1 \left\{ 1 + \frac{2k_p}{k} \arctan \frac{k}{k_i} - \frac{2(k_p - k_i)}{\sqrt{k_i k_p}} \exp \left[ -\frac{k_i}{k} \arctan \frac{k}{k_i} \right] \right\} \quad (17)$$

Equations (16) and (17) can be further simplified, since as we have already mentioned  $k_i \ll k_p$ . In this case, eqs. (16) and (17) become

$$(\overline{M}_n)_\infty \approx M_1 \sqrt{\frac{k_p}{k_i}} \quad (18)$$

and

$$(\overline{M}_w)_\infty \approx (\pi - 2) (\overline{M}_n)_\infty \quad (19)$$

Equations (18) and (19) are both interesting and useful because they relate the degree of polymerization at the end of reaction to the initiation and propagation rate constants.

The arrangement and procedure of our experiment allows continuous measurement of the variation of the monolayer area with time, but it gives no information on the degree of polymerization. Therefore, it is very useful to have expressions that allow the calculation of the degree of polymerization as a function of the area. It is well established that the area per monomer molecule in the monolayer can be expressed as

$$A = A_0 \frac{N_1}{N} + A_\infty \frac{(N - N_1)}{N}$$

or

$$\frac{N_1}{N} = \frac{A - A_\infty}{A_0 - A_\infty} \quad (20)$$

where  $A_0$  is the area per molecule at the beginning of reaction (i.e., just after establishing the pressure) and  $A_\infty$  is the area per molecule at the end.  $A_0$  characterizes the area per monomer molecule and  $A_\infty$  the area per monomer unit in a polymer. Equation (20) can then be used to specify the amount of unreacted monomer,  $N_1$ , using the measured value of  $A$ . In order to relate the value of  $N_1$  to the average molecular weight, eqs. (8),

(10) and (13) are treated as parametric forms of the curves  $(\overline{M}_n)_\infty$  vs.  $N_1$  and  $(\overline{M}_w)_\infty$  vs.  $N_1$ , where the parameter  $\tau$  ranges from 0 to  $\tau_\infty$ . Figure 2 shows  $\overline{M}_w$  against  $N_1$  for different values of  $k_p/k_i$ .

Figure 2.

Thus far the rate equations have been solved in terms of  $\tau$ , and the solution at  $\tau_\infty$ , the reaction end point, has been analyzed. The next step is the consideration of times close to the end of reaction, i.e., for  $\tau_\infty - \tau \ll \tau_\infty$ . In this range,

$$\begin{aligned} N_1(\tau) &\approx N_1(\tau_\infty) + \left[ \frac{dN_1}{d\tau} \right]_{\tau_\infty} (\tau - \tau_\infty) \approx -k_p \theta(\tau_\infty) (\tau - \tau_\infty) \\ &\approx -N \sqrt{k_i k_p} e^{-k_i \tau_\infty} (\tau - \tau_\infty) \end{aligned} \quad (21)$$

By substituting eq. (21) into eq. (14) and subsequent integration, the following approximate relation is obtained:

$$\tau \approx \tau_\infty \left[ 1 - \exp\left(-N \sqrt{k_i k_p} e^{-k_i \tau_\infty} t\right) \right], \quad \tau_\infty - \tau \ll \tau_\infty \quad (22)$$

Note that the integral in eq. (14) runs from  $\tau = 0$  to  $\tau$  and that eq. (21) should only be used for times close to the end of reaction. However, eq. (22) will prove to be a relatively good approximation at any time. (Of course, it will be best at long times.) Figure 3 compares eq. (22) with the result obtained by exact numerical integration of eq. (14) for the case  $k_p/k_i = 100$ . Agreement is obviously very good.

Figure 3.

Equation (22) can be used to determine any of the variables of



interest in terms of  $t$ . Here the (average) barrier speed

$$BS = \frac{A_0 - A_\infty}{W} \left( \frac{dN_1}{dt} \right) \quad (23a)$$

is considered, since it is measured directly in our experiment.<sup>26</sup> In eq. (23a),  $W$  denotes the width of the trough. Using eqs. (22) and (8), eqs. (23a) can be written as

$$BS = \frac{A_0 - A_\infty}{W} \left( \frac{dN_1}{dt} \right) = \frac{A_0 - A_\infty}{W} N_1 (2k_i N_1 + k_p \theta) \quad (23b)$$

It is easy to show that this expression for  $BS$  has a maximum at

$$BS_{\max} \approx \frac{N}{2W} (A_0 - A_\infty) \sqrt{k_i k_p} \left[ 1 + \frac{4 - \pi}{2} \sqrt{\frac{k_i}{k_p}} \right] \approx \frac{N}{2W} (A_0 - A_\infty) k \quad (24)$$

and that the corresponding value of  $\tau$  is

$$\tau_{\max} \approx - \frac{1}{N \sqrt{k_i k_p}} \ln \left[ \frac{1}{2} + \frac{4}{\pi} \sqrt{\frac{k_i}{k_p}} \right] \approx \frac{\ln 2}{N k} \quad (25)$$

Then, the average rate constant can be obtained from the maximum value of the barrier speed as mentioned at the beginning of this section.

However, still more information is needed in order to determine the individual values of the two rate constants. At the beginning of the reaction most of the monomer is still unreacted. Consequently, we can simplify the rate equation for the monomer (first of eqs. 2) by neglecting the second term on the right side of this equation (the term due to propagation). Then, the rate equation becomes

$$\frac{dN_1}{dt} \approx -2k_i N_1^2 \quad \text{when } k_p t \ll 1 \quad (26)$$

and can be integrated to yield

$$N_1 = \frac{N}{1 + 2k_i t} \quad (27)$$

which indicates that a plot of  $N/N_1$  vs.  $t$  during the initial stages of the reaction is a straight line of slope  $2k_i$ . Figure 4 shows such a plot for the experimental data corresponding to a temperature of 25 °C and an applied surface pressure of 10 mN/m. Indeed, the data follow a very good straight line. Once the value of  $k_i$  is obtained by this procedure, the values of  $k$  obtained from eq. (24) can be used to obtain  $k_p$ . Tables I and II show the values of  $k$ ,  $k_i$ , and  $k_p$  at different temperatures derived from the experimental data for surface pressures of 10 mN/m and 20 mN/m, respectively. The rate constants  $k$  and  $k_p$  were calculated using equations 24 and 9, respectively.

Figure 4., Table I, and Table II.

The activation energy for the initiation can now be obtained using the Arrhenius law and plotting  $\ln k_i$  vs.  $1/T$ , as shown in Figure 5. The activation energy for initiation in this plot is  $E_{ai} = 97$  KJ/mol at 10 mN/m applied surface pressure. Equation 24 was used to calculate the activation energy for propagation,  $E_{ap}$ . For this purpose,  $\ln [ W \times BS_{max} / (A_0 - A_{\infty}) ]$  was plotted versus  $1/T$  as shown in Figure 6. The slope of this line is  $[ - (E_{ai} + E_{ap}) / 2R ]$ . Since the value of  $E_{ai}$  is now known,  $E_{ap}$  can be easily computed and found to be 9 KJ/mole at 10 mN/m applied surface pressure. It is interesting to note that if the values of  $k$  were used to

determine the activation energy, we would obtain the arithmetic mean of these two energies, i.e.,  $E_a = 54$  KJ/mol. This average value agrees well with our previously reported value of  $53 \pm 1.5$  KJ/mole calculated from the modified Gee and Rideal equation. Similar calculations were also carried out for the polymerization reaction at 20 mN/m applied surface pressure. Results are summarized in Table III.

Figure 5, Figure 6, and Table III.

Average values of  $E_{ai} + E_{ap}$  match very well, within experimental error, with our previously reported activation energies.<sup>31</sup> Thus the above results indicate that rate constants and activation energies calculated using the modified Gee and Rideal equation were average values. A striking feature, however, is the pressure dependence of the two activation energies. The activation energy for initiation actually decreases slightly with pressure, while that for propagation increases substantially. Since, at a given pressure, persulfate diffusion is likely to be similar near either a propagating chain end or two colliding monomers, it is not likely to be the major cause of this pressure dependence. The number of conformations a chain end can assume, however, is expected to be much different than that for a protonated monomer molecule. The hydration shell around a growing chain end may also be different from that of a protonated monomer. The above considerations suggest that the applied surface pressure primarily affects collisions between monomers and chain ends, by changing the hydration shells and/or their conformations.

It is expected that the average molecular weight at the end of reaction should vary with temperature due to the significant difference

between the initiation and propagation energies. Since eqs. (18) and (19) indicate that these average molecular weights are directly proportional to  $\sqrt{k_p/k_i}$ , and the activation energy for propagation is smaller than for initiation, the average molecular weight must decrease when the temperature is increased. This idea agrees with results obtained by another group<sup>41</sup> in which aniline was polymerized chemically in a homogenous bulk solution. However, certain experimental signatures of the monolayer polymerization are similar to those found in the classical chemical method; our results can be used to support this point of view.

## CONCLUSION

We have presented a simple theoretical model that provides a clear understanding of the kinetics of polymerization in a monolayer. This model agrees very well with our experimental data. Even though the model is in primitive form, it offers clear advantages over those of previous kinetic studies,<sup>31-34</sup> and retains the essential trends of the system. This model also provides some interesting information on the average degree of polymerization, molecular weight, and the fraction of unreacted monomer at any stage during the polymerization reaction. Some predictions concerning the temperature dependence of polymerization are also provided by the model. The rate constant and the activation energy obtained from the modified Gee and Rideal equation have been rationalized as geometric and arithmetic means, respectively, of the values corresponding to the initiation and propagation steps. Finally, even though this model was developed for polymerization of aniline in a monolayer, we believe that it is useful for any solution polymerization having a similar mechanism of propagation.

## ACKNOWLEDGMENT

J. Manzanares thanks the Spanish Ministry of Education and Science for the financial support through a grant of the Fulbright Program. R. Bodalia and R. Duran acknowledge financial support from ONR and technical assistant from KSV Instruments, Finland. R. Bodalia and H. Reiss acknowledge support from NSF grant No. CHE 90-22215.

## REFERENCES

- [1] Gupta, M. C.; Umare, S. S. *Macromolecules* **1992**, *25*, 138.
- [2] Milton, A. J.; Monkman, A. P. *Synth. Met.* **1993**, *57(1)*, 3571.
- [3] Hagiwara, T.; Yamaura, M.; Iwata, K. *Synth. Met.* **1988**, *25*, 243.
- [4] Epstein, A. J.; Ginder, J. N.; Zuo, F.; Bigelow, R. W.; Woo, H. S.; Tanner, D. B.; Ritcher, A. F.; Huang, W. S.; MacDiarmid, A. G. *Synth. Met.* **1987**, *18*, 303.
- [5] Cushman, R. J.; McManus, P. M.; Yang, S. C. *J Electroanal. Chem.* **1986**, *291*, 335.
- [6] Wan, M. J. *J. Polym. Sci., Chem. Ed.* **1992**, *30*, 543.
- [7] Watanabe, A.; Kunio, M.; Iwasaki, Y.; Nakamura, Y.; Niizuma, S. *Macromolecules* **1987**, *20*, 1793.
- [8] Jiang, R.; Dong, S. *Synth. Met.* **1988**, *24*, 255.
- [9] Ohtani, A.; Abe, M.; Ezoe, M.; Dou, T.; Miyata, T.; Miyake, A. *Synth. Met.* **1993**, *57(1)*, 3690.
- [10] Kulkarni, V.; Campbell, J.; Mathew, W. *Synth. Met.* **1993**, *57(1)*, 3780.
- [11] MacDiarmid, A. G.; Mu, S. L.; Somasiri, S. L. D.; Wu, W. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 187.
- [12] Syed, A. A.; Dinesan, M. K. *Synth. Met.* **1990**, *36*, 209.

- [13] Oyama, N.; Oshaka, T.; Shimizu, T. *Anal. Chem.* **1985**, *57*, 1526.
- [14] Anderson, A. R.; Mattes, B. R.; Reiss, H.; Kaner, R. B. *Science* **1991**, *252*, 1412.
- [15] MacDiarmid, A. G.; Chiang, J. C.; Halpern, M.; Huang, W. S.; Mu, S. L.; Somasiri, N. L. D.; Wu, W.; Yaniger S. I. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 173.
- [16] Genies, E. M.; Tsintavis, C.; Syed, A. A. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 181.
- [17] Yun, M. S.; Kang, D. P. *Synth. Met.* **1989**, *29*, E343.
- [18] Inoue, M.; Navarro, R. E.; Inoue, M. B. *Synth. Met.* **1989**, *30*, 199.
- [19] Pron, A.; Genoud, F.; Menardo, C.; Nechtschein, M. *Synth. Met.* **1988**, *24*, 193.
- [20] Leclerc, M.; Guay, J.; Dao, L. *Macromolecules* **1989**, *22*, 649.
- [21] Genies, E. M.; Tsintavis, C. *J. Electroanal. Chem.* **1985**, *195*, 109.
- [22] Wei, Y.; Focke, W. W.; Wnek, G. E.; Ray, A.; MacDiarmid, A. G. *J. Phys. Chem.* **1989**, *93*, 495.
- [23] Genies, E. M.; Boyle, A.; Lapkowski, M.; Tsintavis, C.; *Synth. Met.* **1990**, *36*, 139 and refs. therein.
- [24] Shim, Y.; Won, M.; Park, S. *J. Electrochem. Soc.* **1990**, *137-2*, 538.
- [25] Zhou, H. C.; Batich, C.; Stern, R.; Duran, R. S. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 409.



- [26] Zhou, H. C.; Duran, R. S. *Am. Chem. Soc. Symp. Ser.* **1992**, *31*, 493.
- [27] Duran, R. S.; Zhou, H. C. *Thin Solid Films* **1992**, *210*, 356.
- [28] Duran, R. S.; Zhou, H. C. *Polymer* **1992**, *33-19*, 4019.
- [29] Wei, Y.; Sun, Y.; Tang, X. *J. Phys. Chem.* **1989**, *93*, 4878 and refs. therein.
- [30] Tzou, K.; Gregory, R. V. *Synth. Met.* **1992**, *47*, 267.
- [31] Bodalia, R.; Duran, R. *J. Am. Chem. Soc.* in press.
- [32] Gee, G.; Rideal, E. *Trans. Faraday Soc.* **1935**, *31*, 969.
- [33] Gee, G. *Trans. Faraday Soc.* **1936**, *32*, 187.
- [34] Gee, G. *Proc. Royal Soc., London* **1936**, *A CLIII*, 129.
- [35] Bodalia, R.; Stern, R.; Batich, C.; Duran, R. *J. Polym. Sci., Chem. Ed.* **1993**, *31*, 2123.
- [36] Wei, Y.; Tang, X.; Sun, Y. *J. Polym. Sci., Chem. Ed.* **1989**, *27*, 2385.
- [37] Bodalia, R.; Duran, R. unpublished results.
- [38] Wei, Y.; Jang, G.; Chan, C.; Hsueh, K.; Hariharan, R.; Patel, S.; Whitecar, C. *J. Phys. Chem.* **1990**, *94*, 7716.
- [39] Szymanski, R. *Makromol. Chem.* **1990**, *191*, 933.
- [40] Deyue, Y. *Macromolecules* **1989**, *22*, 2926.

- [41] Klavetter, F.; Cao, Y. unpublished results.

## FIGURE CAPTIONS

- Figure 1. The area and average barrier speed vs. time during the Langmuir film polymerization of 2-pentadecylaniline at 25°C temperature and 20 mN/m applied surface pressure. The sub-phase was a mixture of 0.1M H<sub>2</sub>SO<sub>4</sub> and 0.03M (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. Initial compression speed was 90 Å<sup>2</sup>molecule<sup>-1</sup>min<sup>-1</sup>.
- Figure 2. Weight - average degree of polymerization,  $M_w/M_1$  (continuous lines) and a polydispersity,  $M_w/M_n$ , (dashed lines) vs. the fraction of unreacted monomer  $N_1/N$  as the reaction is taking place. (Note that the abscissa scale has been reversed so that going to the right in the scale means advance in the reaction.) The curves correspond to the following values of  $k_p/k_i$  (from top to bottom): 500, 100, 50.
- Figure 3. Comparison of the exact numerical solution of eq. (14), with  $N_1(\tau)$  given by eq. (8) (continuous line), and the approximate analytical solution shown in eq. (22) (dashed line). The ration  $k_p/k_i$  has been set equal to 100.
- Figure 4. Fraction of unreacted monomer vs. time for the Langmuir film polymerization of 2-pentadecylaniline at 25°C temperature and 10 mN/m applied surface pressure. Data for the first 2.5 minutes of the reaction are shown in this figure.

Figure 5.  $\ln k_i$  vs  $1/T$  ( $^{\circ}\text{K}^{-1}$ ) plot for the monolayer polymerization at 10 mN/m applied surface pressure. A linear regression method was used to draw a straight line from experimental data.

Figure 6.  $\ln [ W \times BS_{\text{max}} / (A_0 - A_{\infty}) ]$  vs.  $T^{-1}$  [ $^{\circ}\text{K}^{-1}$ ] plot for the monolayer polymerization at 10 mN/m applied surface pressure. A linear regression method was used to draw a straight line from experimental data.

Table I. Applied Surface pressure = 10 mN/m.

Temperature [°C]	$k_i$ [min <sup>-1</sup> ]	$k$ [min <sup>-1</sup> ]	$k_p$ [min <sup>-1</sup> ]
15	0.00228	0.0376	0.6224
20	0.00365	0.0506	0.7051
25	0.00832	0.0750	0.6844
30	0.0168	0.1152	0.8067
35	0.0285	0.1608	0.9358
40	0.0528	0.2138	0.9185

**Table II. Applied Surface Pressure = 20 mN/m.**

Temperature [°C]	$k_i$ [min <sup>-1</sup> ]	$k$ [min <sup>-1</sup> ]	$k_p$ [min <sup>-1</sup> ]
10	0.00254	0.0221	0.1945
15	0.00359	0.0326	0.2996
20	0.00705	0.0571	0.4689
25	0.01268	0.0893	0.6420
30	0.02063	0.1394	0.9626
35	0.04548	0.2342	1.2515
40	0.06745	0.3315	1.6967

Table III. A comparison of activation energies obtained by different methods.

Surface Pressure	E <sub>ai</sub> KJ/mole	E <sub>ap</sub> KJ/mole	Average E <sub>a</sub> KJ/mole	E <sub>a</sub> (from ln <i>k</i> vs. 1/T)	E <sub>a</sub> (from Gee Rideal Eq.)
10 mN/m	97	9	53	54 ±1.5	53 ±1.5
20 mN/m	84	50	67	68 ±1.3	66 ±3

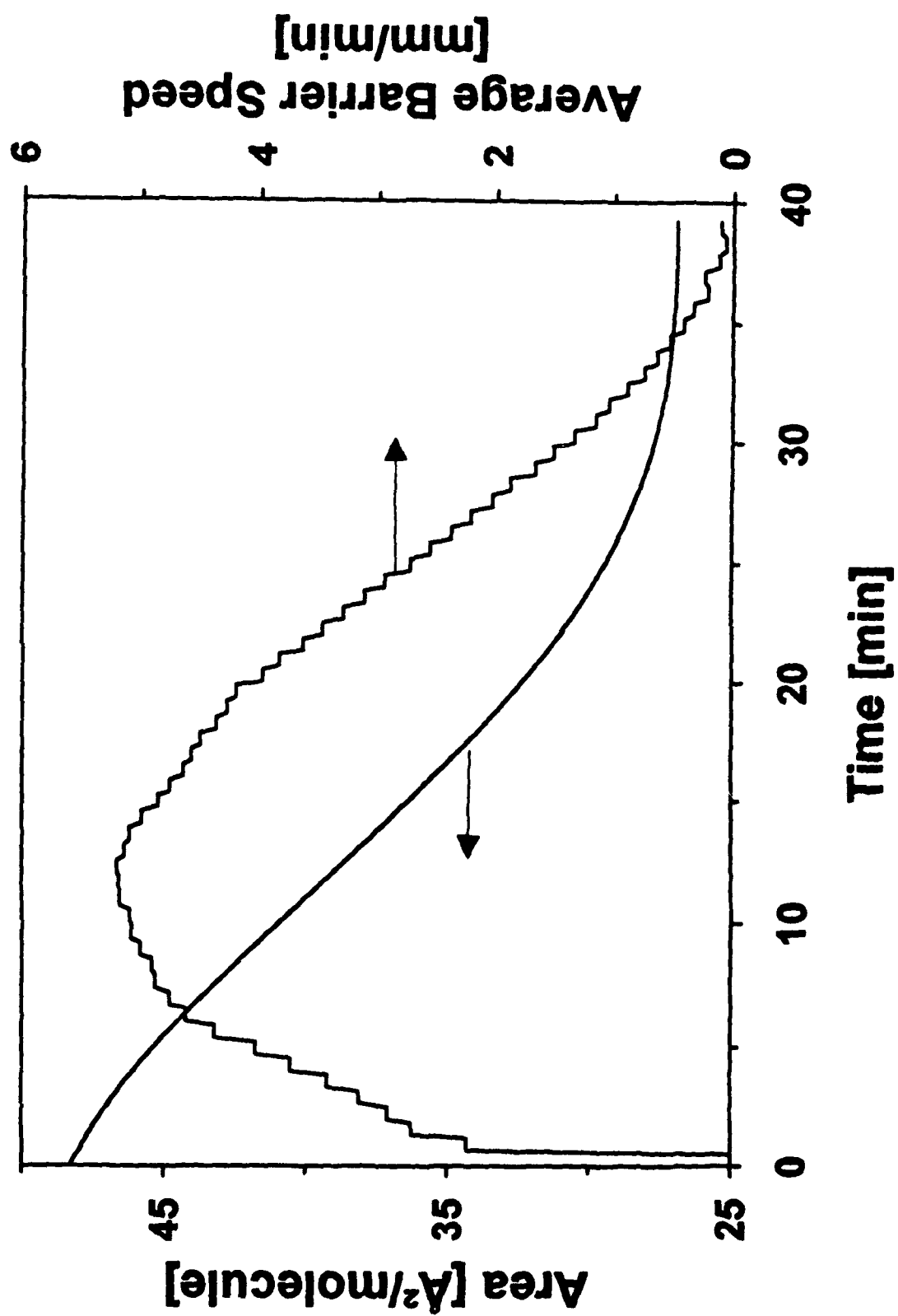


Figure 1.



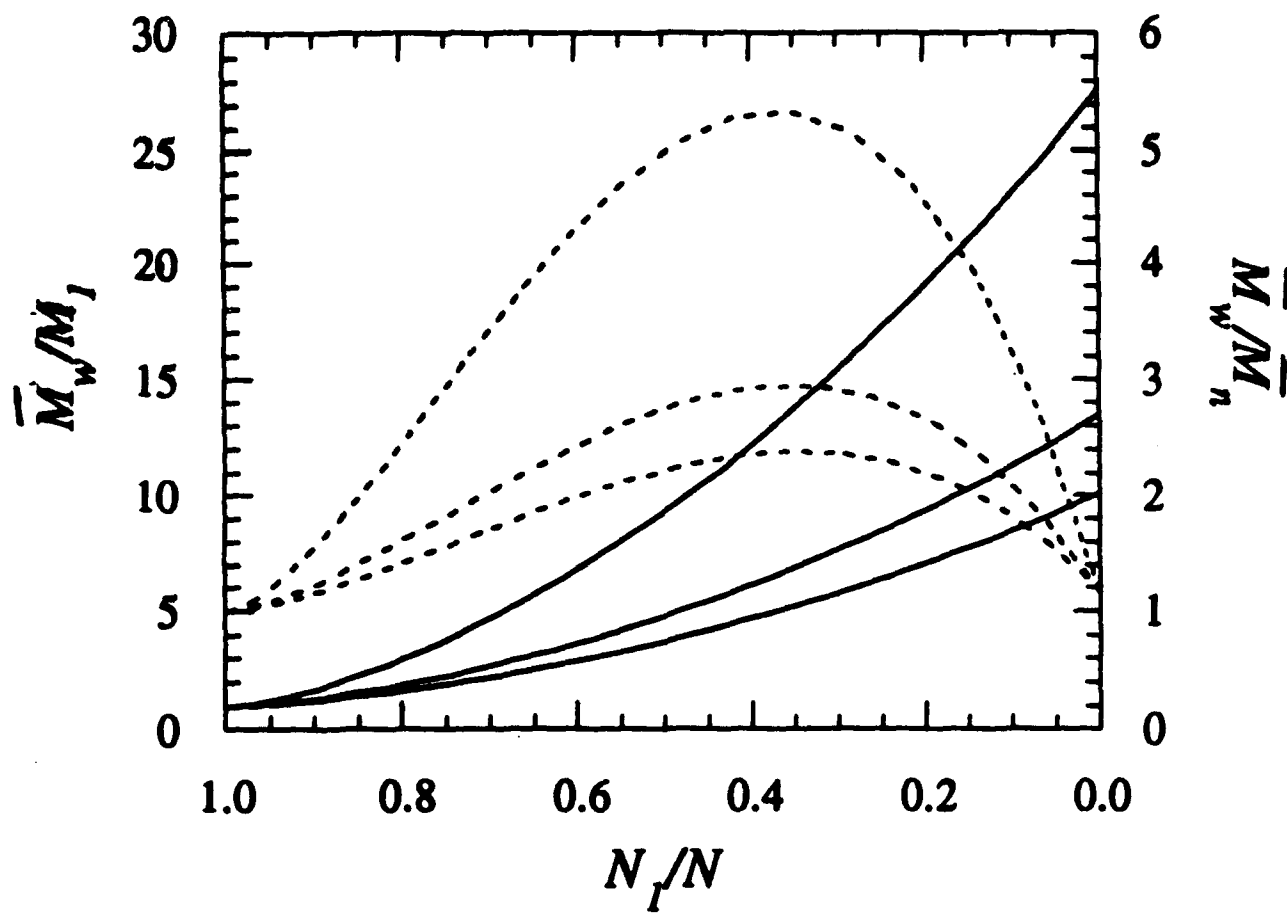


Figure 2.

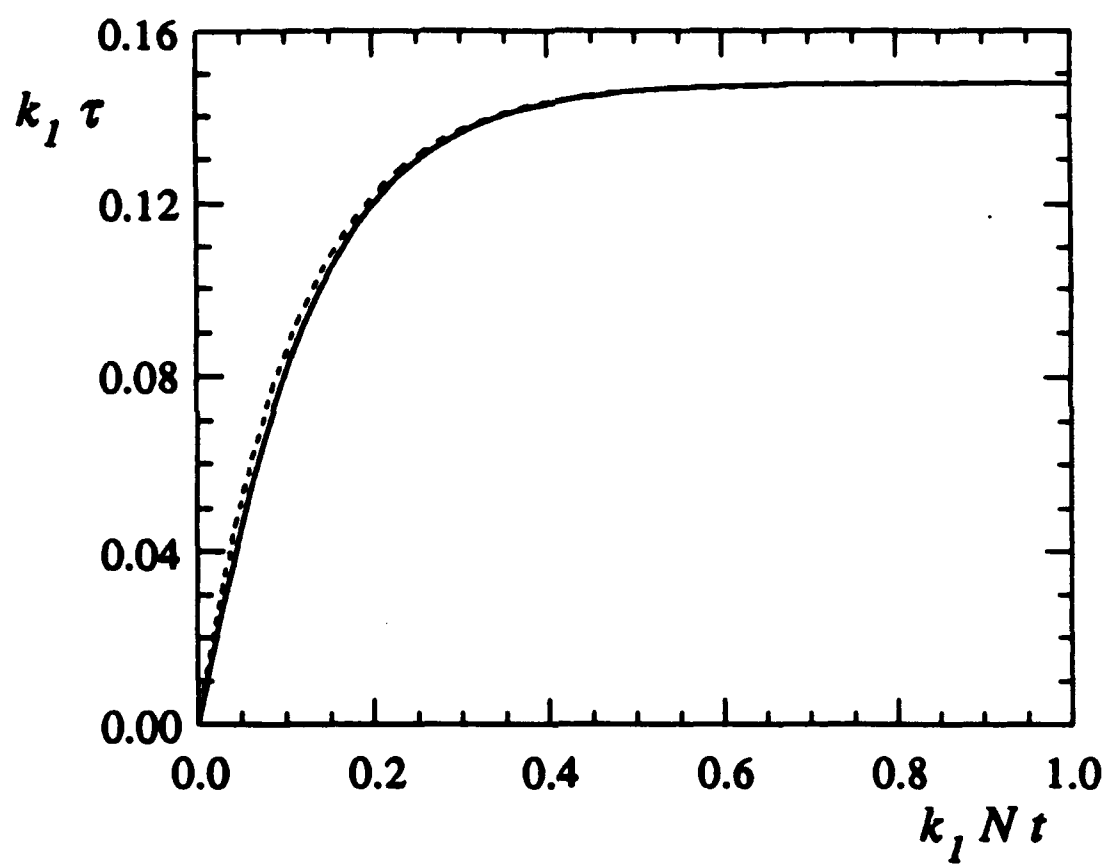


Figure 3.

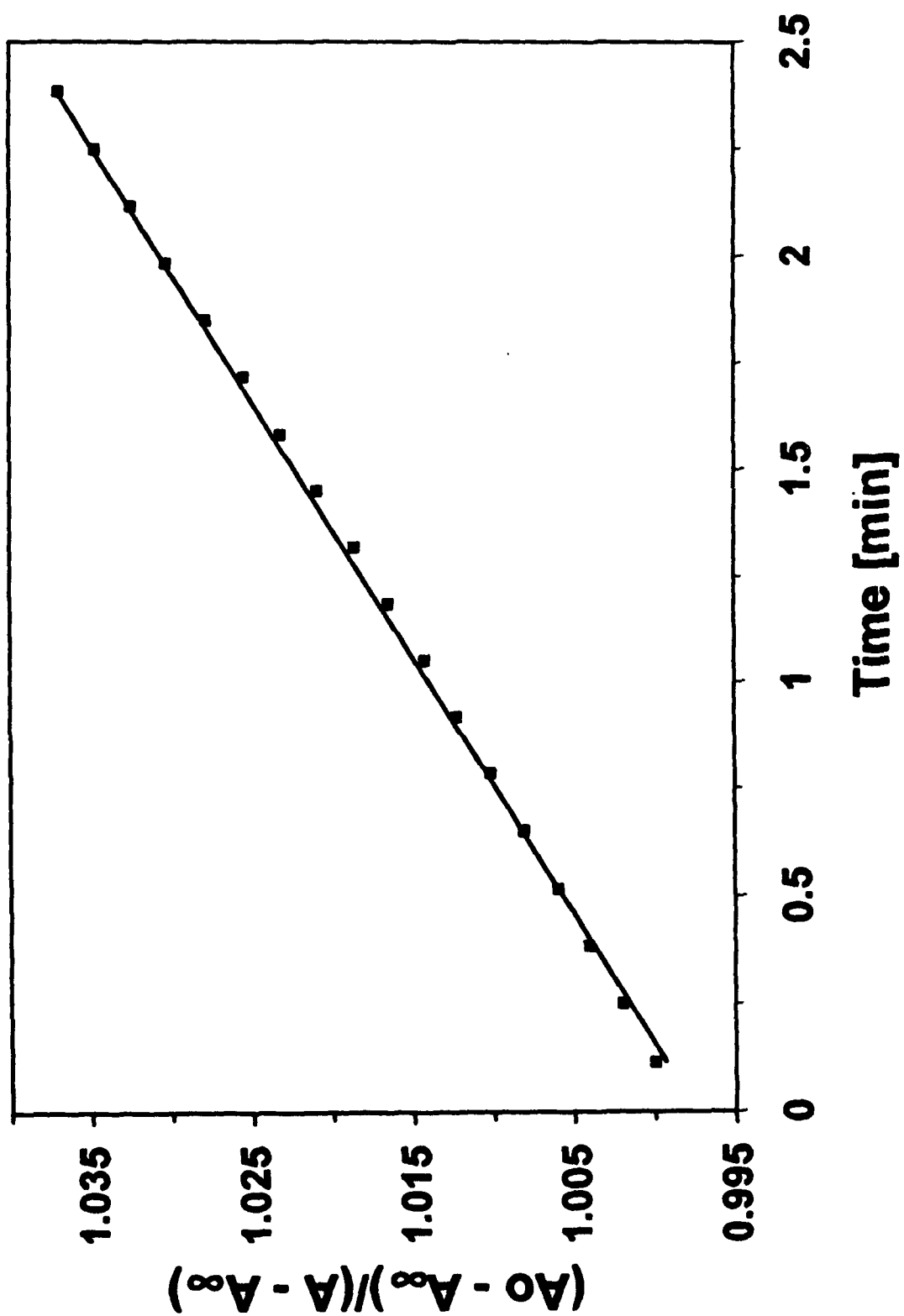


Figure 4

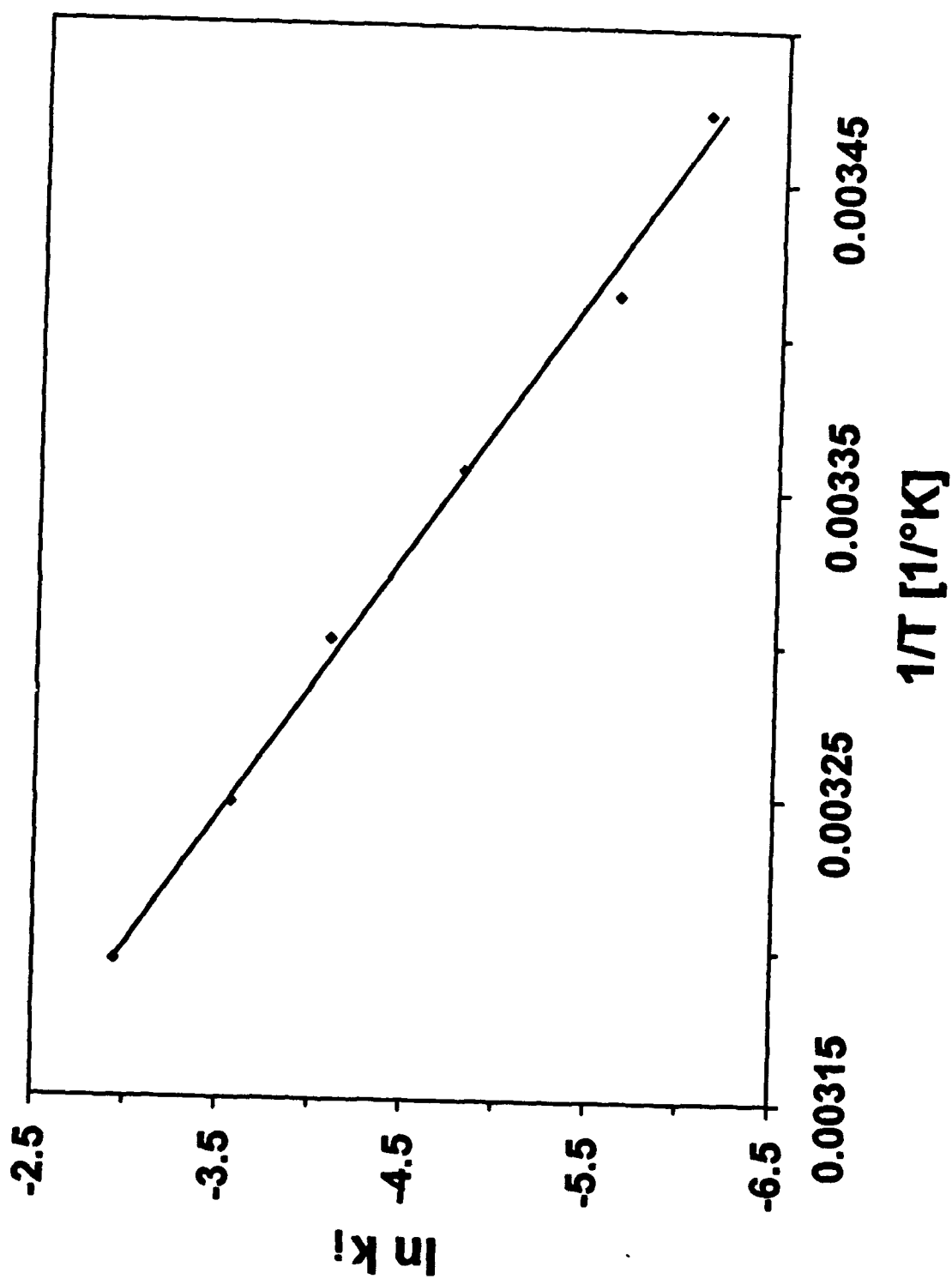


Figure 5.

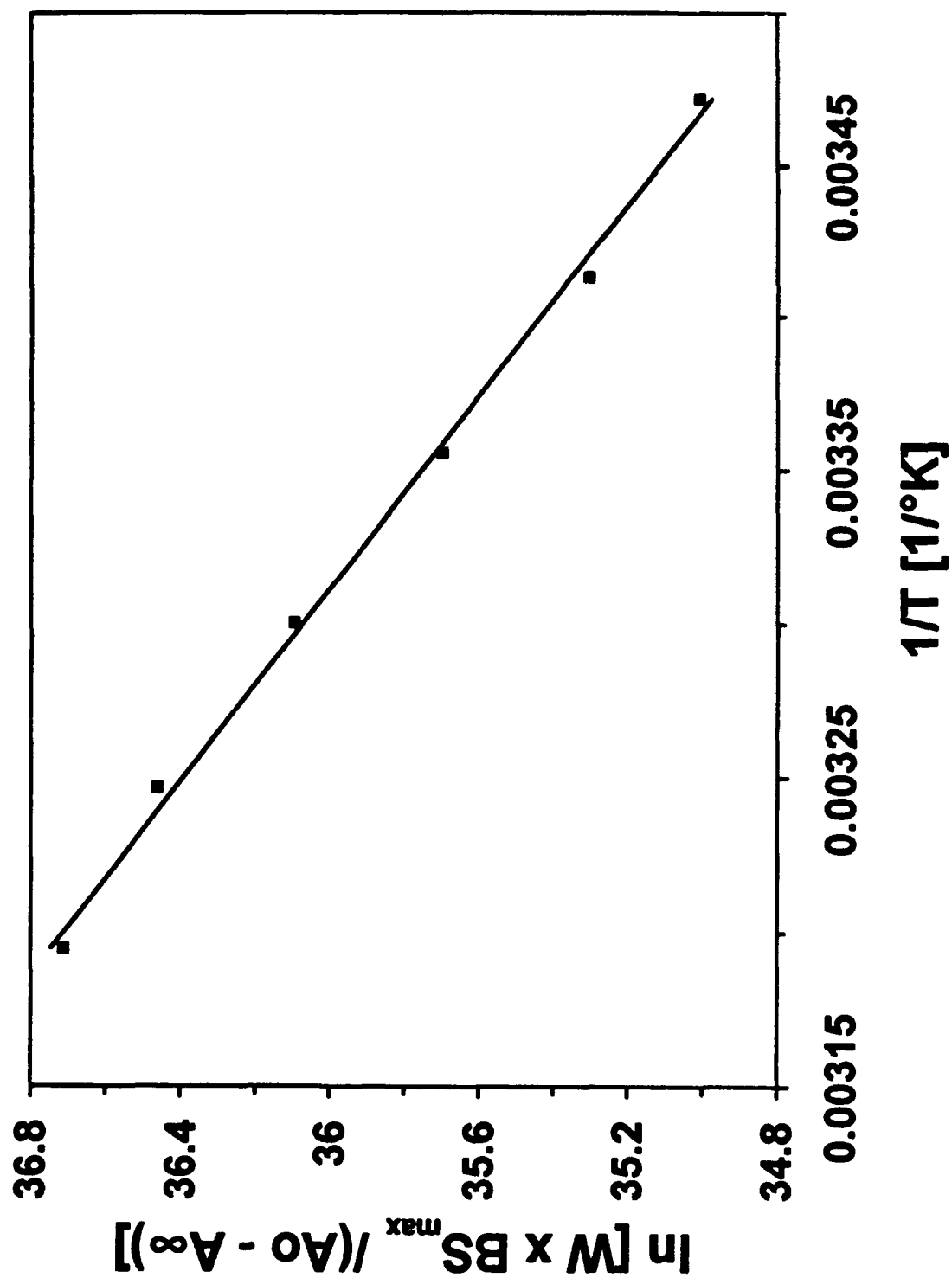


Figure 6

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)  
Chemistry Division, Code 1113  
800 North Quincy Street  
Arlington, Virginia 22217-5000

Dr. Richard W. Drisko (1)  
Naval Civil Engineering  
Laboratory  
Code L52  
Port Hueneme, CA 93043

Dr. James S. Murday (1)  
Chemistry Division, Code 6100  
Naval Research Laboratory  
Washington, D.C. 20375-5000

Dr. Harold H. Singerman (1)  
David Taylor Research Center  
Code 283  
Annapolis, MD 21402-5067

Dr. Robert Green, Director (1)  
Chemistry Division, Code 385  
Naval Weapons Center  
China Lake, CA 93555-6001

Chief of Naval Research (1)  
Special Assistant for Marine  
Corps Matters  
Code 00MC  
800 North Quincy Street  
Arlington, VA 22217-5000

Dr. Eugene C. Fischer (1)  
Code 2840  
David Taylor Research Center  
Annapolis, MD 21402-5067

Defense Technical Information  
Center (2)  
Building 5, Cameron Station  
Alexandria, VA 22314

Dr. Elek Lindner (1)  
Naval Ocean Systems Center  
Code 52  
San Diego, CA 92152-5000

Commanding Officer (1)  
Naval Weapons Support Center  
Dr. Bernard E. Douda  
Crane, Indiana 47522-5050

\* Number of copies to forward